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RELATIVE TOXICITY OF SEVEN OIL-SPILL EMULSIFIERS

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[Toxicite Relative de Sept Produits Emulsionnants Antipetrole]

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INTRODUCTION

There have been a number of products manufactured to treat hydrocarbons spilled onto the surface of the sea accidentally, or chronically. These have been in use for several years, with more or less success. The I.S.T.P.M.* has examined 101 such compounds, of which:

61 of the emulsifier type;

23 of the agglomerant type;

17 of the precipitant type.

The results of the first experimental phase (Alzieu, 1972; Michel, 1972) were the separation of 7 emulsifiers that proved to be efficient when used with petroleum, yet proved to be the least toxic of all emulsifiers tested on the Portuguese oyster (Crassostrea angulata), and on a unicelluar marine alga (Phaeodactylum tricornutum).

This paper will discuss the direct toxicity of these 7 products on several marine animals.

METHODS

The emulsifiers studied are the products designated E_{22}, E_{30}, E_{41}, E_{46}, E_{47}, E_{52}, and E_{53}.

The animals used during the experiments were:

3 gastropods: Gibbula umbilicalis; Purpura lapillus (little purple); and Littorina littorea (winkle);

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* Institute Scientifique et Technique pour la Pêche Maritime [Scientific and Technical Institute of Maritime Fishing].

1 lamellibranch: Mytilus edulis;

3 crustaceans: Artemia salina; Penaeus kerathurus (shrimp); Clinabarius [1] misanthropus (Bernard the hermit);

1 fish: Anguilla anguilla.

The experiments were conducted using batches of 20 to 25 animals placed in 2 liter capacity polyethylene tanks. Aeration was provided by a bubbler in the form of a glass tube with an inside diameter of 1 mm.

In the case of the Artemia salina, we worked with two 10 ml crystallizers for each concentration of the products studied, using 10 adult specimens in each. Aeration was by simple diffusion of the air at the surface of the water. Temperature was maintained very close to 20°C throughout the experiments.

The work done by Portmann and Conner (1968), and by Sprague (1969), showed that many compounds, including emulsifiers, lose their toxic effect, in principle, at the end of 4 days. We adopted this same time frame.

Animals that died during the experiments were removed and counted at the end of 48 and 96 hours. The results were expressed in parts per million by volume (ppm) for each of the 7 emulsifiers causing the death of half the population after 48 and 96 hours of experimentation (LD_{50}). These values were obtained by graphic interpretation of the results.

The emulsifiers were used on adult animals. In the case of mussels, however, practical considerations led us to select those 1 to 2 cm in length. We also used postlarval shrimp measuring 5 to 10 mm in length, as well as young eels with a mean weight of 3 grams.[2]

The Artemiae were obtained by hatching eggs in an Erd-Schreiber medium

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1. Clibanarius DANA.

2. Our thanks to the Department of Works, Research, and Oceanic Exploitation for the shrimp and eels we needed for our experiments.

(Provasoli et al, 1957). They were fed diatom cultures (Phaeodactylum tricornutum and Chaetoceros simplex) and used over a two month period. The emulsifiers were diluted in the Erd-Schreiber medium.

TABLE 1. MOLLUSKS: LD_{50} AFTER 48 and 96 HOURS OF EXPERIMENTATION. VALUES ARE GIVEN IN PARTS OF EMULSIFIER PER MILLION BY VOLUME (PPM).

Emulsionnants Emulsifiers	*Gibbula umbilicalis* LD_{50}		*Purpura lapillus* LD_{50}		*Littorina littorea* LD_{50}		*Mytilus edulis* LD_{50}	
	48 h	96 h	48 h	96 h	48 h	96 h	48 h	96 h
E_{49}	53	72	80	75	320	150	150	104
E_{51}	46	33	26	20	200	145	91	65
E_{41}	35	33	26	20	75	70	37	35
E_{45}	136	39	42	25	550	320	136	118
E_{47}	200	97	200	114	>600	>600	480	305
E_{43}	77	72	26	20	350	300	120	87
E_{53}	110	52	73	52	600	500	540	490

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RESULTS

Table 1 lists the results for LD_{50} for mollusks, and Table 2 those for crustaceans and eels.

It would be ridiculous to attempt an objective classification of the 7 emulsifiers on the basis of their toxicity vis a vis the animals tested. It seems preferable to us to analyze the results as a function of the zoological groups for which they were obtained.

We find that product E_{47} is the least toxic for all 3 species of gastropods tested. Product E_{41}, on the other hand, was definitely toxic

for Gibbula umbilicalis and Purpura lapillus, and less so for Littorina littorea. Product E_{53} is in an advantageous position between these latter two products with respect to the other 4 emulsifiers. Their LD_{50} values are quite close together.

TABLE 2. CRUSTACEANS AND EELS: LD_{50} AFTER 48 and 96 HOURS OF EXPERIMENTATION. VALUES ARE GIVEN IN PARTS OF EMULSIFIER PER MILLION BY VOLUME (PPM).

Emulsionants / Emulsifiers	*Artemia salina* LD_{50}		*Penaeus kerathurus* LD_{50}		*Clinabarius misanthropus* LD_{50}		*Anguilla anguilla* LD_{50}	
	48 h	96 h	48 h	96 h	48 h	96 h	48 h	96 h
E_{22}	31	30	15	8	290	280	150	150
E_{30}	17	13	32	25	410	410	150	150
E_{41}	28	27	22	18	>600	>600	70	70
E_{46}	100	90	73	64	>600	>600	90	90
E_{47}	27	27	240	220	>600	>600	500	500
E_{52}	60	50	77	57	>600	>600	100	100
E_{53}	66	62	65	50	>600	>600	100	100

The LD_{50} value is of the same order of magnitude for Mytilus edulis, but product E_{53} was found to be less noxious, followed closely by product E_{47}, Product E_{41} was found to be most toxic, whereas products E_{46}, E_{22}, E_{52}, and E_{30} were in between.

Crustaceans studied reacted differently to the emulsifiers. The LD_{50} values for Clinabarius misanthropus are quite high for the 7 products, so that any classification would be worthless.

Artemia salina and Penaeus kerathurus on the other hand are more sensitive to oil-spill removers. E_{46} is the product least toxic for the former, and E_{47} for the latter. Product E_{46} shows a lesser toxicity for both species, followed by products E_{52} and E_{53}. Despite its high LD_{50} value for Penaeus kerathurus, product E_{47} has a relative low LD_{50} value for Artemia salina. Products E_{41}, E_{30}, and E_{22} appear to be the products least harmless to these two species.

The LD_{50} value of E_{47} is very high for Anguilla anguilla, and is followed by E_{22} and E_{30}, but their values are plainly of less consequence. Then come products E_{52} and E_{53}, followed by products E_{46} and E_{41}. It should be noted that the eel does not seem to be very sensitive to the emulsifiers tested since all LD_{50} values found are beyond 70 ppm.

Moreover, it should be pointed out that all fatalities were observed during the first day of the experiment.

DISCUSSION

There was never any question of attempting to find out how the emulsifiers tested during these experiments acted. As a matter of fact, these products, the compositions of which were, for the most part, unknown to us, are very different from each other. We thus were limited to a comparative study of their noxiousness toward a few marine animals, of which we were able to bring together about one thousand.

The overall results would appear to show that product E_{47} was the least toxic of the 7 emulsifiers studied, despite the fact that the LD_{50} value was relatively low for Artemia salina.

Well back in the sequence are E_{53} and E_{46}.

The lack of deaths after 24 hours among eels leads us to think that the

toxicity of the 7 emulsifiers is connected with the presence of volatile compounds, most of which would appear to disappear after the medium has been aerated for 24 hours. We concur with Portmann and Connor (1968), Smith (1968), and Lacaze (1969), who had demonstrated the importance of emulsifier solvents in the toxicity observed with respect to animals, as well as diatoms.

But the result observed in the case of the eels ought not be considered a hard and fast rule because, by way of contrast, some products showed increased toxicity for some species between the second and fourth days of the experiment. The toxicity therefore cannot be imputed solely to the solvents, and wetting agents must have a not insignificant part in the baleful effects observed.

CONCLUSIONS

We made what was a purely comparative study of the toxicity of 7 emulsifiers. Our results permit us to say that product E_{47} is the one showing the least overall toxicity so far as the animals studied are concerned: Gibbula umbilicalis, Purpura lapillus, Littorina littorea, Mytilus edulis, Artemia salina, Penaeus kerathurus, Clinabarius misanthropus, and Anguilla anguilla.

Nevertheless, we are very reluctant to write that this product has little toxic effect on marine fauna and flora because there are very great specific variations in the sensitivity of living organisms to pollutants in general, and to anti-spill products in particular.

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